



Condensed Matter and Interphases (Kondensirovannye sredy i mezhfaznye granitsy)

Original article

DOI: <https://doi.org/10.17308/kcmf.2020.22/3120>

Received 30 October 2020

Accepted 15 November 2020

Published online 25 December 2020

ISSN 1606-867X

eISSN 2687-0711

The Synthesis of Nanophosphors $YV_xV_{1-x}O_4$ by Spray Pyrolysis and Microwave Methods

© 2020 E. V. Tomina^{a, b}, D. A. Lastochkin^a, S. A. Maltsev^a

^aVoronezh State University,
1 Universitetskaya pl., Voronezh 394018, Russian Federation

^bVoronezh State University of Forestry and Technologies named after G. F. Morozov,
ul. Timiryazeva, 8, Voronezh 394087, Russian Federation

Abstract

Due to rare earth doping, phosphates and vanadates are the leading materials for the synthesis of phosphors due to their thermal stability, low sintering temperature, and chemical stability. Phosphors in the nanoscale state are of particular interest. The simple, fast, and scalable synthesis of nanophosphors with high chemical homogeneity is a priority task. The purpose of this work was to synthesize powders of mixed yttrium vanadate-phosphate crystals of various compositions by coprecipitation under the action of microwave radiation and spray pyrolysis, as well as to compare the characteristics of the obtained samples.

Samples of $YV_xP_{1-x}O_4$ of different compositions were synthesized by coprecipitation under the action of microwave radiation and spray pyrolysis in different modes. In the case of the synthesis of yttrium vanadate-phosphate $YV_xP_{1-x}O_4$ by spray pyrolysis followed by annealing, according to the X-ray phase analysis data, single-phase nanopowders were formed. The morphological characteristics of the samples were revealed by the methods of transmission electron microscopy and scanning electron microscopy. Depending on the annealing conditions, the samples were either faceted or spherical particles less than 100 nm in size. The composition of the $YV_xP_{1-x}O_4$ samples synthesized by the coprecipitation method under the action of microwave radiation strongly depended on the pH of the precursor solution. The minimum content of impurity phases was reached at pH 9.

Spray pyrolysis allows the synthesis of yttrium vanadate phosphate $YV_xP_{1-x}O_4$ nanopowders of high chemical homogeneity with a particle size of less than 100 nm. The maximum chemical homogeneity of yttrium vanadate-phosphate powders was achieved at pH = 9 during the synthesis of $YV_xP_{1-x}O_4$ by coprecipitation under the action of microwave radiation. However, the particle size dispersion was large, within the range of 2–60 μm.

Keywords: phosphors, microwave synthesis, spray pyrolysis, nanopowders, yttrium vanadate-phosphate.

For citation: Tomina E. V., Lastochkin D. A., Maltsev S. A. The synthesis of nanophosphors $YV_xV_{1-x}O_4$ by spray pyrolysis and microwave methods. *Kondensirovannye sredy i mezhfaznye granitsy = Condensed Matter and Interphases*. 2020;22(4): 496–503. DOI: <https://doi.org/10.17308/kcmf.2020.22/0000>

Для цитирования: Томина Е. В., Ласточкин Д. А., Мальцев С. А. Синтез нанолоюминофоров $YV_xV_{1-x}O_4$ спрей-пиролитическим и микроволновым методами. *Конденсированные среды и межфазные границы*. 2020;22(4): 496–503. DOI: <https://doi.org/10.17308/kcmf.2020.22/3120>

✉ Elena V. Tomina, e-mail: tomina-e-v@yandex.ru



The content is available under Creative Commons Attribution 4.0 License.

1. Introduction

The areas for the application of luminescent materials are diverse: lighting devices, biological markings, plasma panels, and biomedicine [1–4]. Phosphors in the nanoscale state are of particular interest. Phosphates and vanadates are the leading materials for the synthesis of phosphors due to rare earth doping due to their thermal stability, low sintering temperature, chemical stability, and environmental friendliness [5]. Systems of mixed crystals of vanadate-phosphates demonstrate better luminescent properties in comparison with the corresponding vanadates and phosphates [6]. Thus, the quantum yields of europium-doped vanadate phosphate nanoparticles reach 20%, and such mixed crystals can potentially be a red emitting phosphor for PDP [7–9].

Nanophosphors can be synthesized by sol-gel, hydrothermal, and microemulsion methods [10–15]. The use of microwave heating leads to a significant increase in the reaction rate and makes it possible to reduce the synthesis time from several hours or days to several minutes while increasing the purity of the target product [16–18]. The synthesis of nanopowders by aerosol pyrolysis has a number of advantages: high productivity, high purity of the final product, the ability to control morphology and low energy consumption. Aerosol spray pyrolysis (CSP) is in great demand due to its simplicity and low cost [19]. Pyrolytic synthesis products find applications in areas such as catalysis, chromatography, the manufacture of pigments and photoluminescent materials.

The aim of this work was to synthesize mixed crystals of yttrium vanadate phosphate by coprecipitation methods under the action of microwave radiation and spray pyrolysis.

2. Experimental

Vanadium (V) V_2O_5 oxide (AR grade TU 6-09-4093-88), sodium phosphate Na_3PO_4 (AR grade, National product classification code 26 2112 1152 00 GOST 9337-79), yttrium nitrate $Y(NO_3)_3$ (AR grade, CAS 13494-98-9), sodium hydroxide NaOH (AR grade, GOST 432877) served as precursors. For the synthesis of sodium metavanadate, vanadium (V) oxide and sodium hydroxide were mixed in an equivalent ratio, after dissolving them in distilled water. Equivalent amounts of sodium

orthophosphate and yttrium nitrate were added to the resulting solution, exposed to microwave radiation (P_{max} source – 800 W, operating frequency – 2450 MHz) three times within 5 min at 800 W. The pH of the solution was maintained in the range from 7 to 9. The synthesized powder was subjected to ultrasonic dispersion (ultrasonic bath VU-09-“Ya-FP” -0) for 10–15 min. After filtration, the powder was dried for two days, ground in a mortar, and annealed in a muffle furnace (SNOL 8.2/1100) at 800 °C for 1–2 h.

For the synthesis of yttrium vanadate phosphate by the spray pyrolysis method, vanadium (V) oxide V_2O_5 was mixed in an equivalent amount with NaOH to obtain sodium metavanadate ($NaVO_3$). Then, with vigorous stirring, a stoichiometric amount of yttrium nitrate crystalline hydrates $Y(NO_3)_3$, sodium phosphate Na_3PO_4 and concentrated nitric acid HNO_3 (GOST 4461-77) were added for the prevention of the hydrolysis of the solution in the dispersant. The synthesis of nanoparticles was carried out in a spray pyrolysis unit (Fig. 1).

The solution was filled in portions into a disperser, which was connected through branch pipes to a compressor and a quartz tube reactor. The dispersant sprayed the solution in the form of an aerosol into the reactor of the MTP-2M furnace, heated to a temperature of 600 °C. The temperature was controlled by an OVEN TRM1-Shch1.U.R thermostat with an error of ± 1 °C. In the furnace, under the influence of temperature, the aerosol pyrolytically decomposed with the formation of yttrium vanadate phosphate. The nanopowder was collected into a glass with distilled water, then filtered, dried in air, and thermally annealed in a muffle furnace (SNOL 8.2/1100) for recrystallization and complete dehydration at 800 °C for 1–2 hours.

The phase composition of the synthesized powders was determined by X-ray diffraction analysis (XPD) using an ARL X'TRA diffractometer ($Cu K_{\alpha 1}$ with $\lambda = 1.540562$ Å) in continuous mode. The size of the coherent scattering regions (CSR) according to the X-ray diffraction analysis (XPD) data for the samples of yttrium vanadate phosphate was calculated using the Scherrer formula [20]:

$$D_{hkl} = \frac{kx\lambda}{\beta_{hkl} \times \cos\theta}$$

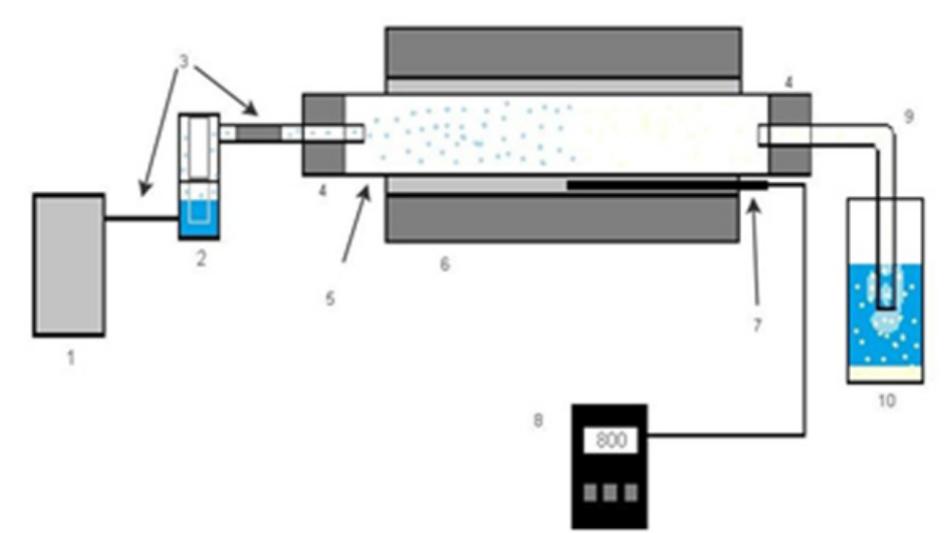


Fig. 1. Installation diagram for the spray pyrolysis: 1 – compressor, 2 – dispersant, 3 – pipes, 4 – rubber stopper, 5 – reactor (quartz tube), 6 – MTP-2M furnace, 7 – thermocouple, 8 – temperature controller, 9 – glass tube with a 90° rotation, 10 – a glass with distilled water for collecting the nanopowder

Where D_{hkl} – average particle size, Å, k – correction factor (for cubic and orthorhombic structure $k = 0.9$), λ – X-ray tube wavelength, θ – the position of the peak maximum, deg., β_{hkl} – intrinsic physical broadening of the diffraction maximum, rad.

The quantitative elemental composition of the synthesized samples was determined by the electron probe X-Ray microanalysis method (EPXMA, scanning electron microscope JEOL-6510LV with a Bruker energy dispersive microanalysis system). The particle size and morphology of the synthesized powders were determined according to transmission electron microscopy (TEM, CarlZeiss Libra-120 transmission electron microscope).

3. Results and discussion

According to the study [6], the stability and high-temperature luminescence properties of doped yttrium vanadates can be improved by a partial replacement of VO_4^{3-} -anions with isostructural anions of PO_4^{3-} . The presence of phosphate anions stabilizes the oxidation state of vanadium +5, which contributes to an increase in the luminescence yield. The doping of the anionic component of yttrium vanadate with smaller anions was accompanied by a decrease in the crystallite size under the same reaction conditions. It seems promising to carry out the synthesis of mixed crystals of yttrium vanadate-phosphate by doping yttrium phosphate with vanadate anions.

The first series of samples of yttrium vanadate phosphates of compositions $YV_{0.1}P_{0.9}O_4$ and $YV_{0.25}P_{0.75}O_4$, synthesized under the action of microwave radiation followed by ultrasonic dispersion, mainly contained the YPO_4 phase. However, reflections of vanadium oxides VO_2 and yttrium Y_2O_3 were revealed on diffractograms of $YV_{0.1}P_{0.9}O_4$ (Fig. 2). Changing the pH of the solution from 7 to 9 decreased the content of impurities in the synthesized powders of yttrium vanadate phosphate (Fig. 3). For $YV_{0.25}P_{0.75}O_4$ samples synthesized at pH 8, vanadium VO_2 and yttrium Y_2O_3 oxides were detected as the main impurity phases (Fig. 2). The reflections of these oxides were not differentiated in the diffractogram with an increase in the pH of the precursor solution from 8 to 9 (Fig. 3).

As a result of the synthesis of yttrium vanadate phosphate of the compositions $YV_{0.1}P_{0.9}O_4$ and $YV_{0.25}P_{0.75}O_4$ by spray pyrolysis without subsequent annealing, samples, containing a mixture of phases: yttrium oxide Y_2O_3 , vanadium oxides VO_2 , V_2O_5 , and sodium vanadates were formed. The high background suggests a rather high degree of amorphism of the samples. The diffraction pattern of $YV_{0.1}P_{0.9}O_4$ sample synthesized by spray pyrolysis and annealed in a muffle furnace at 800 °C for 1 h (Fig. 4a) contained reflections of only yttrium phosphate. The small width of the reflections suggests a high degree of crystallinity of the sample. An increase in the annealing time up to 2 h (Fig.4b) was accompanied by an

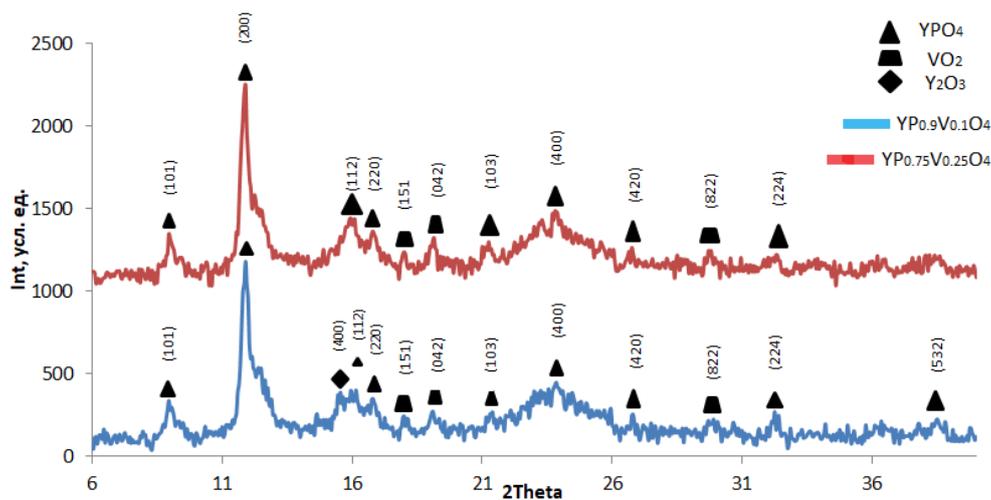


Fig. 2. X-ray diffractograms of the samples, microwave synthesis: a) $YV_{0.1}P_{0.9}O_4$ (pH = 7); b) $YV_{0.25}P_{0.75}O_4$ (pH = 8)

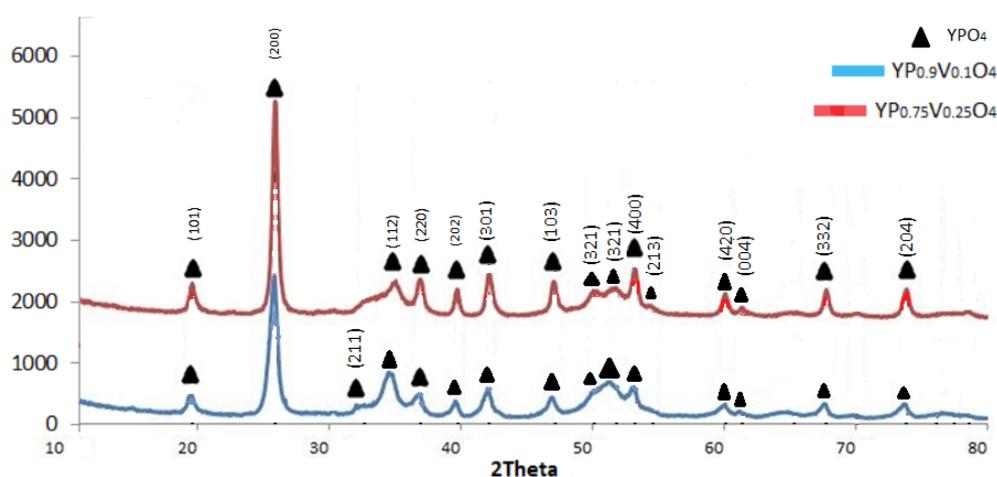


Fig. 3. X-ray diffractograms of $YV_{0.1}P_{0.9}O_4$ samples, microwave synthesis, pH = 9: a) $YV_{0.1}P_{0.9}O_4$; b) $YV_{0.25}P_{0.75}O_4$

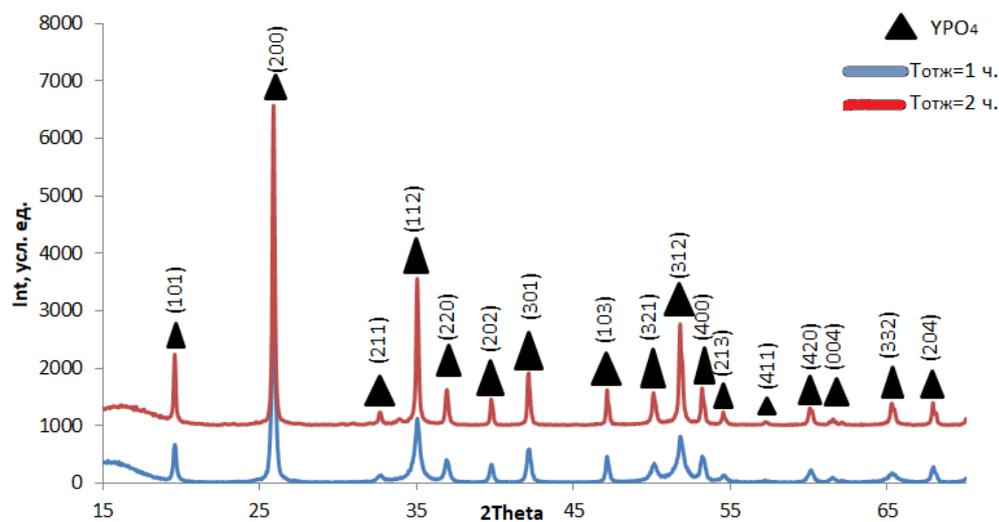


Fig. 4. X-ray diffractograms of $YV_{0.1}P_{0.9}O_4$ samples annealed: for a) 1 h and b) 2 h

increase in the intensity of reflections of YPO_4 . The absence of vanadium-containing compounds in the diffractograms indicated the incorporation of vanadium in the form of vanadate ions into the crystal lattice of yttrium phosphate. The average CSR of particles of the $YV_{0.1}P_{0.9}O_4$ sample annealed for 1 h was 50 ± 2 nm (Table 1). Annealing for 2 h led to an increase in CSR up to 93 ± 2 nm.

On the energy dispersive spectrum of the $YV_{0.25}P_{0.75}O_4$ sample synthesized by the coprecipitation method under the influence of microwave radiation at pH 7, only Y, P, and O signals were recorded (Fig. 5a). Apparently, the incorporation of V^{5+} ions into the YPO_4 lattice

did not occur in a neutral solution, which was also confirmed by the XRD data regarding the presence of various vanadium oxides as impurities in these samples. An increase in the pH of the precursor solution to 8 allowed recording the vanadium signals in the energy dispersive spectrum (Fig. 5b). However, their intensity was low, the actual composition of the sample with respect to vanadium deviated by almost an order of magnitude from the nominal composition (Table. 2). Obviously, only partial incorporation of the introduced V^{5+} ions into the YPO_4 lattice occurred, the majority of vanadium ions were present in the form of impurity oxides. Only an

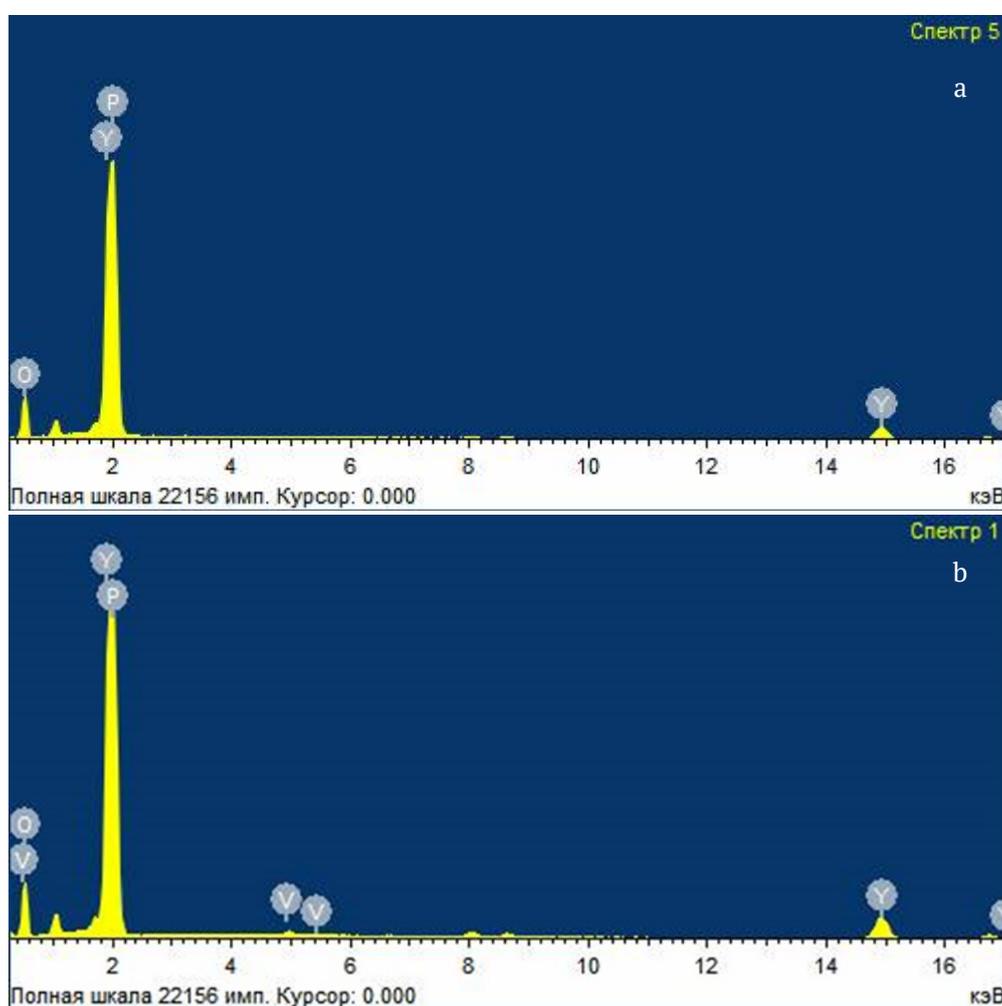


Fig. 5 Energy dispersion spectrum of samples: a) $YV_{0.25}P_{0.75}O_4$ (pH = 7); b) $YV_{0.25}P_{0.75}O_4$ (pH = 8)

Table 1. The radius of coherent scattering region of $YV_{0.1}P_{0.9}O_4$ samples with different annealing times

Sample	D_1	D_2	D_3	D_{cp}
$YV_{0.1}P_{0.9}O_4$ sample ($t_{ann} = 1$ h)	27 ± 1	41 ± 2	54 ± 3	41 ± 2
$YV_{0.1}P_{0.9}O_4$ sample ($t_{ann} = 2$ h)	99 ± 2	73 ± 2	106 ± 2	93 ± 2

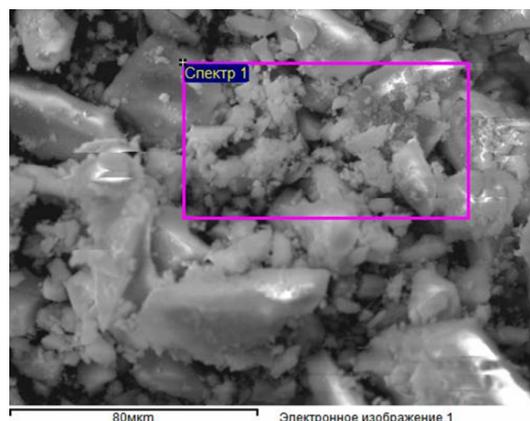
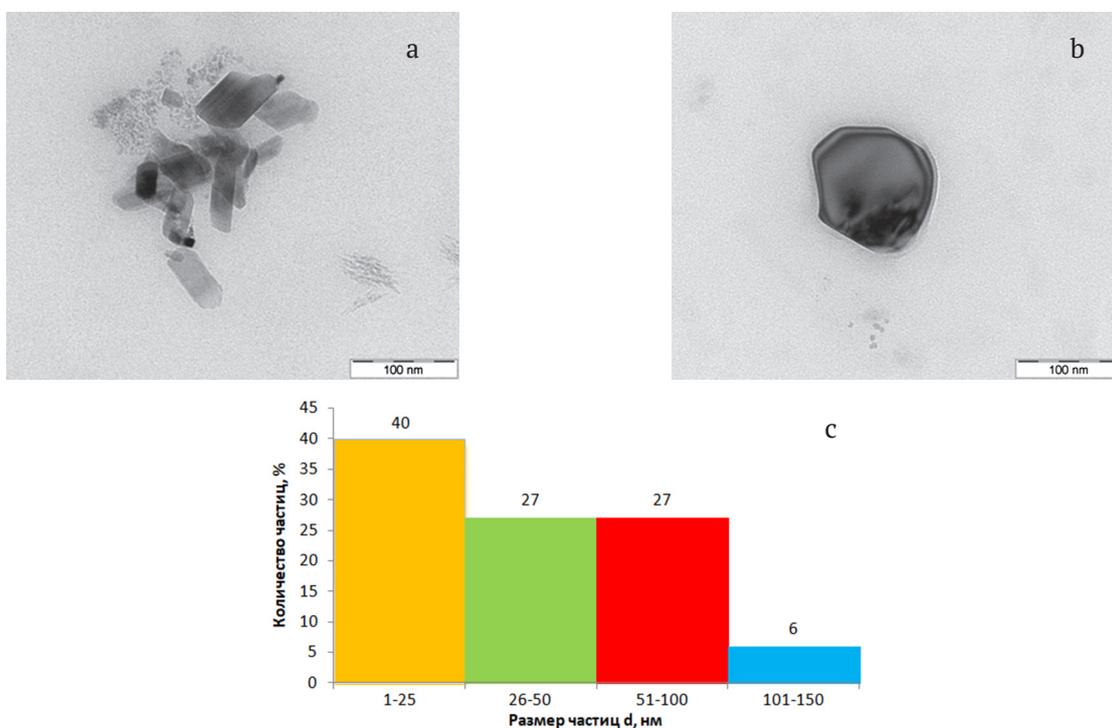
Table 2. Data on the elemental composition of vanadate phosphates (pH = 7, pH = 8, pH = 9)

Nominal composition of samples	$YV_{0.1}P_{0.9}O_4$, pH = 7	$YV_{0.25}P_{0.75}O_4$, pH = 8	$YV_{0.25}P_{0.75}O_4$, pH = 9
Y (nominal), at%	16.6	16.6	16.6
Y (real), at%	11.94	12.2	16.18
V (nominal), atm. %	1.6	4.16	4.16
V (real), at%	0.1	0.24	5.97
P (nominal), atm. %	15	12.5	12.5
P (real), at%	13.74	13.78	11.42
O (nominal), at%	66.6	66.6	66.6
O (real), at%	74.22	73.77	64.31
Real composition of samples	$YV_{0.008}P_{1.15}O_{6.21}$	$YV_{0.02}P_{1.15}O_{6.17}$	$YV_{0.36}P_{0.68}O_{3.97}$

increase in pH to 9 allowed synthesizing samples, the real composition of which was close to the nominal (Table 2).

Morphologically, samples of yttrium vanadate phosphate synthesized by coprecipitation under the action of microwave radiation at pH = 8 were represented by large formations with an arbitrary shape up to 60 μm and smaller amorphised particles from 2 to 10 μm (Fig. 6).

According to TEM data (Fig. 7), $YV_{0.1}P_{0.9}O_4$ synthesized by spray pyrolysis and annealed at 800 $^{\circ}\text{C}$ for 1 h were faceted, had a size in the range of 25–100 nm, and weakly expressed agglomeration was observed (Fig. 7a). An increase

**Fig. 6.** SEM image of $YV_{0.25}P_{0.75}O_4$ powder synthesized by co-deposition under the action of microwave radiation (pH = 8)**Fig. 7.** TEM image of $YV_{0.1}P_{0.9}O_4$ sample in a gelatin layer: a) annealing at 800 $^{\circ}\text{C}$, 1 h; b) annealing at 800 $^{\circ}\text{C}$, 2 h; c) histogram of the particle size distribution of $YV_{0.1}P_{0.9}O_4$ sample

in the annealing time to 2 h promoted the formation of larger spherical particles (Fig. 7b).

4. Conclusions

It was established that the spray pyrolysis method with subsequent annealing allowed synthesizing nanopowders of yttrium vanadate phosphate of high chemical homogeneity with a size in the range of 20–100 nm with a low degree of agglomeration. The change of the annealing mode allowed controlling the size and shape of the particles.

The synthesis of $Y V_x P_{1-x} O_4$ by the coprecipitation method under the action of microwave radiation due to the high sensitivity to pH of the precursor solution was accompanied by the presence of impurity phases in the samples. The maximum chemical homogeneity of yttrium vanadate phosphate powders was achieved at pH = 9. The particle size dispersion was large and was in the range of 2–80 μm .

References

1. Wu C., Wang Y., Jie W. Hydrothermal synthesis and luminescent properties of $\text{LnPO}_4:\text{Tb}$ (Ln = La, Gd) phosphors under VUV excitation. *Journal of Alloys and Compounds*. 2007;436: 383–386. DOI: <https://doi.org/10.1016/j.jallcom.2006.07.056>
2. Huang J., Tang L., Chen N., Du G. Broadening the photoluminescence excitation spectral bandwidth of $\text{YVO}_4:\text{Eu}^{3+}$ nanoparticles via a novel core-shell and hybridization approach. *Materials*. 2019;12: 3830. DOI: <https://doi.org/10.3390/ma12233830>
3. Wu Y., Zhang Z., Suo H., Zhao X., Guo C. 808 nm light triggered up-conversion optical nanothermometer $\text{YPO}_4:\text{Nd}^{3+}/\text{Yb}^{3+}/\text{Er}^{3+}$ based on FIR technology. *Journal of Luminescence*. 2019;214: 116478. DOI: <https://doi.org/10.1016/j.jlumin.2019.116578>
4. Xiu Z., Wu Y., Hao X., Li X., Zhang L. Uniform and well-dispersed $\text{Y}_2\text{O}_3:\text{Eu}/\text{YVO}_4:\text{Eu}$ composite microspheres with high photoluminescence prepared by chemical corrosion approach. *Colloids Surf. A*. 2012;401(5): 68–73. DOI: <https://doi.org/10.1016/j.colsurfa.2012.03.021>
5. Vats B. G., Gupta S. K., Keskar M., Phatak R., Mukherjee S., Kannan S. The effect of vanadium substitution on photoluminescent properties of $\text{KSrLa}(\text{PO}_4)_x(\text{VO}_4)_{2x}:\text{Eu}^{3+}$ phosphors, a new variant of phosphovanadates. *New Journal of Chemistry*. 2016;40(2): 1799–1806. DOI: <https://doi.org/10.1039/c5nj02951a>
6. Riwozki K., Haase M. Colloidal $\text{YVO}_4:\text{Eu}$ and $\text{YP}_{0.95}\text{V}_{0.05}\text{O}_4:\text{Eu}$ nanoparticles: luminescence and energy transfer processes. *The Journal of Physical Chemistry B*. 2001;105(51): 12709–12713. DOI: <https://doi.org/10.1021/jp0113735>
7. Wu C.-C., Chen K.-B., Lee C.-S., Chen T.-M., Cheng B.-M. Synthesis and VUV photoluminescence characterization of $(\text{Y,Gd})(\text{V,P})\text{O}_4:\text{Eu}^{3+}$ as a potential red-emitting PDP phosphor. *Chem. Mater.* 2007;19(13): 3278–3285. DOI: <https://doi.org/10.1021/cm061042a>
8. Shimomura Y., Kurushima T., Olivia R., Kijima N. Synthesis of $\text{Y}(\text{P,V})\text{O}_4:\text{Eu}^{3+}$ red phosphor by spray pyrolysis without postheating. *The Japan Society of Applied*. 2005;44(3): 1356–1360. DOI: <https://doi.org/10.1143/JJAP.44.1356>
9. Lai H., Chen B., Xu W., Xie Y., Wang X., Di W. Fine particles $(\text{Y,Gd})\text{P}_x\text{V}_{1-x}\text{O}_4:\text{Eu}^{3+}$ phosphor for PDP prepared by coprecipitation reaction. *Materials Letters*. 2006;60(11): 1341–1343. DOI: <https://doi.org/10.1016/j.matlet.2005.11.051>
10. Singh V., Takami S., Aoki N., Hojo D., Arita T., Adschiri T. Hydrothermal synthesis of luminescent $\text{GdVO}_4:\text{Eu}$ nanoparticles with dispersibility in organic solvents. *Journal of Nanoparticle Research*. 2014;16(5): 2378. DOI: <https://doi.org/10.1007/s11051-014-2378-2>
11. Song W.-S., Kim Y.-S., Yang H. Hydrothermal synthesis of self-emitting $\text{Y}(\text{V,P})\text{O}_4$ nanophosphors for fabrication of transparent blue-emitting display device. *Journal of Luminescence*. 2012;132(11): 1278–1284. DOI: <https://doi.org/10.1016/j.jlumin.2012.01.015>
12. Yu M., Lin J., Fu J., Han Y. Sol-gel fabrication, patterning and photoluminescent properties of $\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$ nanocrystalline thin films. *Chemical Physics Letters*. 2003;5(1-2): 178–183. DOI: [https://doi.org/10.1016/S0009-2614\(03\)00239-2](https://doi.org/10.1016/S0009-2614(03)00239-2)
13. Raoufi D., Raoufi T. The effect of heat treatment on the physical properties of sol-gel derived ZnO thin films. *Applied Surface Science*. 2009;255(11): 5812–5817. DOI: <https://doi.org/10.1016/j.apsusc.2009.01.010>
14. Shao J., Yan J., Li X., Li S., Hu T. Novel fluorescent label based on $\text{YVO}_4:\text{Bi}^{3+}, \text{Eu}^{3+}$ for latent fingerprint detection. *Dyes and Pigments*. 2019;160: 555–562. DOI: <https://doi.org/10.1016/j.dyepig.2018.08.033>
15. Dolinskaya Yu. A., Kolesnikov I. E., Kurochkin A. V., Man'shina A. A., Mikhailov M. D., Semencha A. V. Sol-Gel synthesis and luminescent properties of $\text{YVO}_4:\text{Eu}$ nanoparticles. *Glass Physics and Chemistry*. 2013;39(3): 308–310. DOI: <https://doi.org/10.1134/s1087659613030061>
16. Tomina E. V., Sladkoptev B. V., Knurova M. V., Latyshev A. N., Mittova I. Y., Mittova V. O. Microwave synthesis and luminescence properties of $\text{YVO}_4:\text{Eu}^{3+}$. *Inorganic Materials*. 2016;52(5): 495–498. DOI: <https://doi.org/10.1134/S0020168516050174>
17. Tomina E. V., Mittova I. J., Burtseva N. A., Sladkoptev B. V. Method for synthesis of yttrium

orthovanadate-based phosphor: patent for invention No 2548089. The patent holder FGBOU VPO “Voronezh state University” No 2013133382/05; declared 12.11.2013; published. 20.05.2015.

18. Tomina E. V., Kurkin N. A., & Mal'tsev S. A. Microwave synthesis of yttrium orthoferrite doped with nickel. *Kondensirovannyye sredy i mezhfaznye granitsy = Condensed Matter and Interphases*. 2019;21(2): 306–312. DOI: <https://doi.org/10.17308/kcmf.2019.21/768> (In Russ., abstract in Eng.)

19. Huang J., Gao R., Lu Z., Qian D., Li W., Huang B., He X. Sol-gel preparation and photoluminescence enhancement of Li⁺ and Eu³⁺ co-doped YPO₄ nanophosphors. *Optical Materials*. 2010;32(9): 857–861. DOI: <https://doi.org/10.1016/j.optmat.2009.12.011>

20. Brandon D., Kaplan W. D. *Microstructural Characterization of Materials*. John Wiley & Sons Ltd; 1999. 409 p. DOI: <https://doi.org/10.1002/9780470727133>

Acknowledgements

The research results were partially obtained were obtained using the equipment of Shared Scientific Equipment Centre of Voronezh State University. URL: <http://ckp.vsu.ru>.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

Information about the authors

Elena V. Tomina, DSc in Chemistry, Associate Professor, Voronezh State University, Voronezh State University of Forestry and Technologies named after G. F. Morozov, Voronezh, Russian Federation; e-mail: tomina-e-v@yandex.ru. ORCID iD: <https://orcid.org/0000-0002-5222-0756>.

Dmitry A. Lastochkin, 1st year Master's degree student Voronezh State University, Voronezh, Russian Federation; e-mail: lastochkin.d1998@mail.ru

Sergey A. Maltsev, 2nd year Master's degree student, Voronezh State University, Voronezh, Russian Federation; e-mail: sergmaltsev97@mail.ru

All authors have read and approved the final manuscript.

Translated by Valentina Mittova

Edited and proofread by Simon Cox